

Final Report

CONCENTRATIONS OF CARBON MONOXIDE  
AND ORGANIC GASES IN ARCTIC ATMOSPHERES

Prepared for:

HEAD, ARCTIC PROGRAM  
EARTH SCIENCES DIVISION  
OFFICE OF NAVAL RESEARCH  
DEPARTMENT OF THE NAVY  
WASHINGTON, D. C. 20360

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REQUISITION NO. NR 307-313 2-13-67  
(CODE 415)

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

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April 1968

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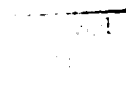
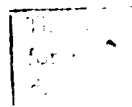
*By:* LEONARD A. CAVANAGH

*SRI Project PRU-6689*

*Approved:* N. K. HIESTER, DIRECTOR  
CHEMICAL DEVELOPMENT AND ENGINEERING DIVISION

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## I. INTRODUCTION

During this research program measurements were made of concentration patterns of low molecular weight organic gases and carbon monoxide (CO) as a function of the meteorological and other parameters in "clean" Arctic air masses. The investigation was conducted at the Naval Arctic Research Laboratory (NARL), Point Barrow, Alaska.

In present technical literature there is considerable information on polluted atmospheres, but relatively little is known about the minor components of the rural or unpolluted atmosphere. Junge,<sup>1</sup> for example, simply indicates that it is possible that other hydrocarbons beside methane are present in the atmosphere because they are known to be produced by plants and perhaps by natural gas leakage. The north Arctic slope is an ideal location for the study of clean atmospheres because settlements can be avoided and there are few combustion sources or vehicles to produce atmospheric contaminants. In addition, the technical support facilities available at NARL are excellent.

Originally, this research program was to include measurements of CO and organics during the fall season, coinciding with freezing of the tundra and during the spring thaw. The University of Washington has made CO<sub>2</sub> measurements for several years at Point Barrow.<sup>2</sup> Their records indicate that atmospheric CO<sub>2</sub> levels are minimal during August and September and maximal during April and May. The changes in CO<sub>2</sub> concentration are attributed to the growth cycle of the Arctic flora.

The program was planned to coincide with the latter part of the growing season of tundra flora and with the usual period of the annual minimum concentrations of CO<sub>2</sub> in the atmosphere. This was done so that hopefully over a longer period of study, possible correlations with CO<sub>2</sub>

and processes in the biosphere could be obtained. Although the present single sampling period was too short to permit any such correlations to be developed, it is hoped that future work along these lines can be conducted and explanations developed for the observed patterns.

## II. FIELD PROGRAM

This research program was designed to include measurements during the last two weeks of August and the first two weeks of September, 1967. However, the flood that occurred in Fairbanks on August 14, 1967, delayed the shipment of compressed gases required for the gas chromatography until late in August. The carbon monoxide analyzer was also delayed in transit. Both CO and organic analysis instrumentation, however, was in operation during the last week of August and through September 11.

The instruments employed in the study for measuring organics and CO were located in a wanigan one mile south of the NARL complex to reduce the likelihood of local contamination from that source. A new technique developed at Stanford Research Institute for CO analysis was used to monitor the atmospheric CO,<sup>3</sup> and gas chromatography was used to analyze low molecular weight hydrocarbons. Methane concentration was monitored with a hydrogen flame ionization detector which has an activated carbon filter. The concentration of submicroscopic particles in the atmosphere was measured with a General Electric condensation nuclei counter.

The majority of the air samples for organic analysis were obtained at the laboratory site, but some air samples were also collected using glass sample bottles during air trips to Meade River and Peard Bay, which are located 50 miles south and 50 miles southwest of Point Barrow, respectively. The samples were taken back to the wanigan laboratory for hydrocarbon analysis.

### Analysis Procedures

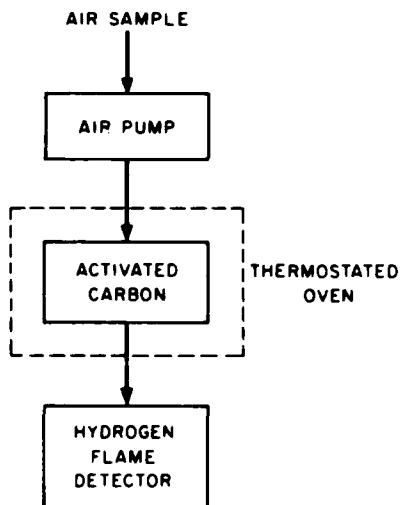
#### Carbon Monoxide Analysis

The continuous measurement of CO in clean atmospheres is feasible because of the sensitivity of the CO detection instrument which was developed by Robbins et al.<sup>3</sup> and has been in use for several years at SRI in studies of clean atmospheres.

This carbon monoxide analyzer uses a rapid quantitative reaction between CO and hot mercuric oxide (HgO). The chemically produced mercury vapor is then measured by standard UV absorption spectroscopy using the strong 2537 Å line. The HgO cell design provides for very low background mercury vapor from thermal dissociation. Therefore, the analyzer is capable of extreme sensitivity and changes in CO concentration of 2 parts per billion (ppb) may be measured. The HgO cell, in combination with a series silver oxide oxidation cell (to provide a base or reference mercury vapor level), is sensitive to olefins and aldehydes. However, these are normally present in the ambient atmosphere in very low concentrations relative to CO. Hydrogen and methane in the atmosphere do not interfere with the CO analysis.

#### Methane Analysis

The methane concentration was determined by a hydrogen flame detector using a continuous sample air flow. This methane determination is similar to that described by Altshuller and coworkers.<sup>4</sup> One channel of a dual-channel Varian Aerograph Model 204B was used as the methane analyzer. A schematic diagram of the methane analysis procedure is shown in Fig. 1.



TA-6689-1

FIG. 1 SCHEMATIC DIAGRAM OF METHANE ANALYZER

The sample air was drawn through a port located about 12 feet above the ground. The air sample is pumped into the analyzer by a diaphragm pump using check valves and a diaphragm fabricated from Teflon. This Teflon-metal construction reduces the possibility of contamination of the sample air by the pump. Prior to sample introduction into the flame detector, the air passes through a bed of activated charcoal maintained at 30°C. This bed of charcoal removes all organics except methane.



Periodic calibration of the methane analyzer at Point Barrow was accomplished by substituting compressed air with a known methane content for outside air at the sample inlet to the methane analyzer. The methane content of the calibration air was determined at the SRI laboratory in Menlo Park prior to the field program.

#### Organic Analysis

The concentrations of low molecular weight hydrocarbons were determined by gas chromatography. The second channel of the dual-channel Varian Aerograph Model 204B, in conjunction with a special inlet system, was used for these analyses. The gas chromatograph was modified to permit either a 6-foot 20% Carbowax 20M or a 6-foot Porapak Q column to be valved in tandem with the organic analysis detector.

It was necessary to concentrate the organic components from the atmosphere in the inlet system by means of a cryogenically cooled freeze-out trap prior to sample release into the separation column. The inlet system contains two injection ports and their associated cryogenic freeze-out traps. The freeze-out traps are packed with Carbowax 20M and Porapak Q to concentrate the atmospheric organics prior to release into their respective gas chromatographic columns.

The Carbowax 20M separation column is used to determine the  $C_2$  to  $C_{10}$  organics. The Porapak Q column was designed to provide a separate means of measuring the methane content of the atmosphere and to allow increased resolution and accuracy in the determination of  $C_2$  to  $C_4$  alkanes and alkenes. The Porapak Q column did not prove to be feasible at Point Barrow because the very low concentrations of  $C_2$  to  $C_4$  hydrocarbons were obscured by tailing of the large methane peak. Therefore, the organic determinations were accomplished primarily using the Carbowax 20M separation column and concentration trap.

The air samples were obtained by gas-tight syringes from a windward location outside the wanigan and about 1 meter above the ground. A 200-milliliter sample of air was used for gas chromatographic analysis. This represented four fillings of a 50 cc syringe taken over a period of

about 2 minutes. This relatively large sample was needed because the majority of the organic contaminants was present at concentrations of 1 ppb or less.

Helium was used as the carrier gas for the gas chromatograph. The gas chromatographic column was maintained at 78° to 82°C. Liquid oxygen was used as the cryogenic fluid. Although liquid oxygen could not be conveniently shipped to Point Barrow, it was condensed at the site as required from compressed oxygen cooled by liquid nitrogen. Separate hydrogen supplies were used for the methane analyzer and the gas chromatograph.

Detector sensitivity was determined by periodic calibration using acetone vapor in equilibrium with liquid acetone at a known temperature. Detection sensitivities for other organics relative to acetone sensitivity were also determined. Retention time calibration was accomplished using vapor in equilibrium with a standard mixture containing pentane, acetone, methane, benzene, and toluene. Although only 1 microliter of calibration standard was required, this quantity far exceeded the concentration of most organic components of the atmosphere. These relatively concentrated calibration standards did not completely elute from the cryogenic freeze-out trap during the initial thermal release. During succeeding heating and cooling cycles minute quantities of the calibration standard were eluted. Therefore, prior to atmospheric analysis, 200 milliliters of helium carrier gas was injected into the gas chromatograph to determine the concentration of helium impurities and the magnitude of the cryogenic trap "memory." This background, if any, was subtracted from the atmospheric sample.

The air samples taken at areas remote from the laboratory were collected in 1-liter Pyrex bottles with Teflon stopcocks. The bottles were returned to the laboratory at NARL for analysis.

#### Condensation Nuclei

The concentration of submicroscopic particles in the atmosphere is, in general, a measure of contamination. Salt particles resulting from the evaporation of salt water droplets contribute to the number of

condensation nuclei in the atmosphere; however, combustion processes represent the major source of condensation nuclei. The concentration of particles in the Arctic atmosphere was measured by a Rich expansion-type condensation nuclei counter.\* The air samples collected near NARL contained 10,000 to 50,000 particles per cubic centimeter (N/cc) because of the numerous combustion sources within the complex. The concentration of nuclei in uncontaminated Arctic air near our wanigan laboratory varied from an undetectable level to 200 N/cc.

The calibration of a photoelectric nuclei counter such as the one used in this program is based on the work of Nolan and Pollak.<sup>5</sup> Although the SRI counter has been calibrated relative to a Sholz counter, no calibration points were obtained at nuclei concentrations as low as that present in the Arctic atmosphere and the data presented are our extrapolation of prior calibrations at concentrations greater than 900 CN/cc.

#### Sampling Results

Table I lists the concentration of CO in parts per billion and the concentration of condensation nuclei in particles per cubic centimeter observed in the Arctic atmosphere. Table II lists the CO concentrations, the methane concentrations, the nuclei concentrations, and the concentration of five organic components of major interest at representative times during the daily sampling program. Table III lists all of the organic components, major and minor, the detected gas chromatographically as well as methane, CO, and condensation nuclei determined on an hourly basis during a 24-hour analysis period from September 2 to 3. The 24-hour run was designed to explore possible diurnal changes in the concentration of contaminants in Arctic air.

The most apparent anomaly in the results listed in Tables II and III is the extremely high concentration of n-butanol relative to the concentration of other constituents. It was recognized in the field that this component was present in unusually high concentration. The

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\* General Electric Company, Type CN.

Table I  
CARBON MONOXIDE DATA  
Point Barrow, Alaska  
August 24-September 11, 1967

Date	Hour	Concentration (ppb)	Condensation Nuclei (N/cc)
8/24/67			300
8/25/67	1540	173	200
	1630	90	
	2050	134	
	2100	63	
	2115	72	
	2140	55	
	8/26/67	1120	
1140		84	
1145		84	
1150		84	
1355		55	
1420		62	50
1510		98	
1550		74	
1620		88	
1710		113	50
1715		113	
1730		126	
8/27/67		Wind from Barrow Village--possible contamination	
8/28/67	1050	55	300 300
	1605-1630	100	
	1635-1655	112	
	1710-1725	116	
	1745-1820	116	
8/29/67	1140-1210	240	up to 2000 } Vehicles up to 2000 } upwind
	1220-1235	180	
	1330-1350	260	
	1445-1500	190	
	1520-1610	165	
	1630-1650	215	
8/30/67	1100-1115	115	300
	1145-1155	100	100
	1500-1510	100	300
	1530-1555	85	
	1610-1650	100	
	1700-1720	80	300

Table I (Continued)

Date	Hour	Concentration (ppb)	Condensation Nuclei (N/cc)
8/31/67	1520-1530	250	200
	1645-1700	100	200
9/1/67	0920-1020	80	50
	2115-2140	130	50
9/2/67	1030	122	0
	1040	94	
	1050	132	
	1130	89	
	1150	102	
	1210	83	
	1230	64	
	1300	152	
	1315	158	0
	1330	146	
	1410	140	0
	1450	125	
	1545	134	0
	1600	126	
	1630	105	0
	1700	120	0
	1740	127	
	1820	102	100
	1900	119	
	1920	102	
	1940	119	
	2000	93	
	2120	102	
	2230	119	0
	2300	85	
	2340	100	
	2400	100	
9/3/67	0020	107	
	0040	81	
	0140	80	
	0200	112	
	0220	119	
	0240	141	200

Table I (Concluded)

Date	Hour	Concentration (ppb)	Condensation Nuclei (N/cc)
9/5/67	0310	115	100
	0330	123	
	0350	146	
	0500	90	
	0530	97	
	0610	89	
	0650	110	
	0700	89	
	0740	105	
	0830	105	
	0900	114	0
	0930	92	0
	1110	76	500
	1200	68	
	1210	71	
	1230	67	
	1300	67	
	1330	66	
	1400	71	50
	1445	83	
	1500	83	
	1535	71	
	1550	71	
	1620	85	
9/6/67	1125-1145	150	50
	1315-1335	110	
	1420-1500	95	
	1615-1730	95	200
9/8/67	1020-1045	75	50
	1120-1215	80	0
	1230-1345	95	
	1430-1530	80	0
	1535-1605	70	
	1650-1735	60	
9/9/67	1600-1630	80	
	1700-1715	80	
	1740-1810	60	
9/11/67	0810-0830	115	100
	0920-0950	80	100
	1000-1030	75	100

<sup>a</sup> Interpolated values

Table II  
CARBON MONOXIDE AND MAJOR ORGANIC COMPONENTS OF THE ATMOSPHERE  
Point Barrow, Alaska  
August 25-September 11, 1967

Date	Hour	CO (ppb)	CH <sub>4</sub> (ppm)	Ethane <sup>a</sup> Ethylene (ppb)	Butane (ppb)	Unknown (1) (ppb)	Acetone (ppb)	Butanol (ppb)	Condensation Nuclei (N/cc)
8 25 67	1540	173							
	2140	55							
8 26 67	1140	84							50
	1420	62							50
	1730	126							50
8 28 67	1050	55							
	1605	100							300
	1745	116							
8/29/67	1140	240							
	1520	165							2000
	1630	215							
8 30 67	1100	115	1.65						300
	1130			0.04	0.04	1.0	0.6	91	100
	1300		1.71						
	1500	100	1.70						
	1730	80		0.06	0.05	1.2	0.7	242	300
8 31 67	0945		1.68						
	1000			0.02	0.02	1.3	0.04	48.8	
	1200		1.71						
	1645	100							200
9 1 67	0910	80	1.50						50
	0930			0.02	0.01	1.0	0.02	34.2	
	1200		1.56						
	1430			0.05	0.06	2.6	1.0	85.6	
	1530		1.62						
	1640			0.05	0.04	2.0	1.0	95.0	
	2000		1.60						
	2115	130							50
9 2 67	See Table III for detailed results								
9 3 67									
9 4 67	1145		1.64						
	1205		1.59	0.03	0.05	3.1	1.2	171	
	1550			0.09	0.11	1.8	0.9	333	
	1630		1.58						
	1645			0.06	0.06	1.8	1.1	300	
	1705			0.06	0.1	1.3	1.0	265	
9 5 67	1110	76							
	1210	71	1.60						500
	1230	67		0.05	0.02	3.1	1.4	185	
	1445	83		0.08	0.02	2.4	1.6	265	50
	1535	71		0.07	0.06	2.9	N.D.	445	
	1550	71							300
	1605			0.09	0.14	2.9	0.5	438	
	1725			0.08	0.09	2.5	1.1	376	
9 6 67	1125	150							50
	1430		1.6						
	1500	95		0.06	0.08	3.6	0.8	282	
	1600	95		0.06	0.19	4.9	1.9	301	200
	1715		1.5						

Table II (Concluded)

Date	Hour	CO (ppb)	CH <sub>4</sub> (ppm)	Ethane <sup>a</sup> Ethylene (ppb)	Butane (ppb)	Unknown (1) (ppb)	Acetone (ppb)	Butanol (ppb)	Condensation Nuclei (N/cc)
9 8 67	1020	75	1.6	0.07	0.04	2.4	0.6	150	50
	1200	80	1.55	0.08	0.08	2.6	1.1	202	0
	1520	80		0.06	0.13	1.5	0.6	219	0
	1650	60	1.58						
9 9/67	1740	60		0.02	0.03	1.3	0.5	49	
9 11 67	0820	115	1.6	0.03	0.03	1.1	0.3	59	100
	0840			0.04	0.06	1.1	0.4	65	
	1030	75	1.51						100
9/8/67									
Meade River #1		80		0.05	N.D.	4.8	1.0	128	100
Meade River #4			1.57						100
Meade River #6		70		0.04	0.05	2.9	1.0	139	
Meade River #3		60		0.05	0.06	3.4	0.9	231	100
Meade River #2		80							100
Meade River #5		60							100
Peard Bay #1		85		0.04	0.06	2.8	0.4	68	
Peard Bay #2		85		N.D.	0.2	2.8	0.4	57	

<sup>a</sup> composite peak.

N.D. = no data.



Table III  
CARBON MONOXIDE AND ORGANICS IN THE ATMOSPHERE, PT. BARROW, ALASKA  
24-Hr. Analysis, September 2-3, 1967

Date	Time	Ethane <sup>a</sup> Ethylene ppb	Butane ppb	Pentane ppb	Unknown (1) ppb	Acetaldehyde ppb	Acetone ppb	Unknown (2) ppb	Methanol Ethanol ppb	Benzene ppb	Unknown (3) ppb	Unknown (4) ppb	n-Butanol ppb	Methane ppm	Carbon Monoxide ppb	Conden- sation Nuclei N/cc
9 2 67	1030	0.04	0.19	0.1	2.3	0.2	1.6	0.3	b	b	0.4	b	96	1.4	122	0
9 2 67	1110	0.01	0.05	N.D.	3.0	0.3	N.D.	0.2	0.5	b	0.4	0.2	96	1.52	89	
9 2 67	1230	0.03	0.04	N.D.	3.3	0.3	1.5	0.2	0.5	b	b	0.5	73	N.D.	64	
9 2 67	1310	b	b	N.D.	6.9	0.2	2.7	0.3	0.9	b	0.4	0.1	91	1.52	146	0
9 2 67	1410	0.03	b	N.D.	9.1		2.9	0.5	b	b	0.4	0.3	91	1.41	125	
9 2 67	1500	0.03	0.03	N.D.	3.4	0.3	1.9	0.2	b	b	0.3	0.2	81	1.4	N.D.	
9 2 67	1550	0.06	0.08	N.D.	1.8	0.1	0.9	b	0.7	b	b	b	97	1.46	134	0
9 2 67	1630	0.05	0.06	N.D.	1.6	b	0.9	b	b	b	b	0.3	111	N.D.	105	
9 2 67	1730	0.08	0.11	N.D.	1.6	b	1.3	0.2	1.2	b	0.4	0.2	126	1.39	127	
9 2 67	1820	0.06	0.04	N.D.	1.2	b	1.1	b	b	b	0.5	0.2	121	N.D.	102	100
9 2 67	1930	0.03	0.04	N.D.	1.1	b	0.3	b	0.9	b	0.4	0.3	83	1.43	119	
9 2 67	2050	0.06	0.08	N.D.	0.4	b	N.D.	b	0.9	b	0.4	0.2	99	1.35	N.D.	0
9 2 67	2115	0.03	0.05	N.D.	0.4	b	N.D.	b	b	b	0.2	0.2	83	1.35	102	
9 2 67	2230	0.06	0.06	0.09	0.2	b	0.8	b	0.7	b	b	0.4	76	N.D.	119	0
9 2 67	2330	0.05	0.03	0.1	0.3	b	0.9	b	0.9	b	0.3	0.3	74	N.D.	100	
9 3 67	0030	0.05	0.05	0.2	0.3	b	1.2	b	0.9	0.1	0.4	0.3	68	N.D.	107	
9 3 67	0130	0.02	0.03	0.1	0.3	b	0.9	b	0.9	b	0.3	b	57	N.D.	80	
9 3 67	0230	0.05	0.05	0.2	0.3	b	1.0	0.4	0.4	0.4	0.2	b	51	N.D.	119	200
9 3 67	0330	0.04	0.03	0.1	0.3	b	0.7	b	0.4	0.1	0.3	b	73	1.48	123	100
9 3 67	0430	0.05	0.05	N.D.	1.1	0.3	0.7	b	b	b	0.3	b	86	1.50	90	
9 3 67	0530	0.05	0.03	0.2	0.5	b	1.1	b	0.7	0.1	0.4	b	107	1.50	97	
9 3 67	0630	0.04	0.04	0.3	0.9	b	0.9	b	0.7	0.1	0.3	b	83	N.D.	110	
9 3 67	0730	0.04	0.1	0.08	1.4	b	1.0	b	0.7	b	0.3	b	93	1.55	105	
9 3 67	0830	0.06	0.1	N.D.	1.4	b	1.1	b	0.7	b	0.4	b	92	1.55	105	0
9 3 67	0930	0.05	0.1	N.D.	1.7	b	1.3	b	0.9	b	0.4	b	90	1.65	92	0

<sup>a</sup> Composite peak.

b Not detected.

N.D. - no data, instrument difficulties.

n-butanol elutes from a Carbowax 20M column under our operating parameters at an elution time similar to toluene. Since toluene was a component of our calibration elution standard mixture and because it was an unexpected component in these clean Arctic air samples, considerable effort was made to assure that the peak was not the result of faulty technique or contaminated sampling equipment. As part of our test program the gas-tight sample syringes were used to inject carrier gas into the inlet system of the gas chromatograph. The carrier gas did not contain any detectable component having the elution time of n-butanol; neither did the syringe used for injection contain any detectable n-butanol. The gas-tight sample syringes were also baked for 12 hours at 125°C to remove organic contaminants. Air samples taken prior to baking contained organic components comparable to samples taken after baking.

The possibility of this peak resulting from atmospheric oxygen contacting and decomposing the hot Carbowax 20M column liquid phase was considered. This possibility was discounted when no peak resulted from injection of 80% carrier helium and 20% oxygen.

Samples were collected at areas remote from Point Barrow to determine the organic components of air not subject to local contamination. Before taking samples the collection bottles were flushed first with helium and then with ambient air. Gas chromatograms of the air within the bottles after this flushing indicated that no organic components were being contributed by the flasks themselves. Air samples were collected at Meade River and Peard Bay after flushing the bottles with about six volumes of air. These remote samples contained n-butanol at concentrations comparable to those found at Point Barrow. This would certainly indicate that the presence of n-butanol was not due to local contamination in the vicinity of the laboratory wanigan.

The n-butanol peak could not be identified from retention times using the Carbowax 20M and SE-30 liquid phase columns available at Barrow. Therefore, bottle samples were taken at Barrow and returned to the Menlo Park laboratories of SRI to provide substantiating identification information. Ambient air samples were also taken in Menlo Park, using

all of the same equipment used in the field studies at Point Barrow. Although the ambient air of Menlo Park contains considerably higher concentrations of a broad range of organics, n-butanol was not present in concentrations comparable to those at Point Barrow. In another set of check analyses the Point Barrow sample collection bottles were used to collect two samples of "clean" air from the windward coast of Kauai, Hawaii. The same gas chromatographic equipment and conditions were used for analysis. Neither sample of Hawaiian air contained detectable concentrations of n-butanol.\*

From bottle samples collected at Point Barrow, the major component was identified as n-butanol rather than toluene by gas chromatographic retention times observed on Carbowax 20M and diglycerol liquid phase columns and on a solid absorption column of Porapak Q. Although it is not possible to unequivocally identify an organic by gas chromatography alone, the possibility is extremely remote that this major contaminant could possess the identical retention time as an n-butanol standard on three different separation columns and not be n-butanol.

The organics other than n-butanol listed in Tables II and III represent tentative identification based on gas chromatographic retention times observed with a Carbowax 20M liquid phase column.

The concentration of organics listed in Tables II and III was calculated with the detector sensitivity for the listed compounds except for the following: ethane-ethylene used butane calibration for detector sensitivity; and acetaldehyde, benzene, and all unknowns used detector sensitivity calibration for acetone.

The preliminary results given in Status Report No. 1, Table I, issued October 24, 1967, on SRI Project No. PAU-6689, listed the concentrations of all organics based on the detector sensitivity of acetone. At the time Status Report No. 1 was issued, n-butanol had not been identified and is listed as the last unknown peak in the column adjacent to methane.

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\* SRI Notebook No. 8832, p. 132.

Another change has been made in Status Report No. 1, Table I, with regard to the column of tabulated ethane concentrations. Subsequent work has shown that this peak was the result of a partial retention of methane and does not represent the actual ethane concentration. It has now been established that ethane and ethylene could not be resolved under the field operating conditions. Therefore, ethane and ethylene are tabulated in Table III of this final report as a composite peak.

### Discussion of Results

#### Carbon Monoxide

The carbon monoxide concentration in the Arctic atmosphere was quite low and varied from 55 to 260 ppb. The CO concentration usually varied less than 20 ppb during any given day, and the concentration was usually within the range of 50 to 150 ppb with an average of 90 ppb. In general, the CO concentrations at Point Barrow were consistently low and less varied than that measured previously in clean atmospheres. The concentration of atmospheric CO at Point Barrow is considerably lower than that measured during a recent SRI study at a remote location on the Greenland ice cap.<sup>6</sup> During late July and early August 1967, the data gathered 400 miles east-northeast of Thule, Greenland, at Inge Lehmann Station (78 N, 39 W) indicated an average atmospheric CO concentration of 200 ppb with a low of 60 ppb and a high of 500 ppb.

There is some evidence in biological literature that CO may be liberated by growing plants.<sup>7</sup> If this were a major source of atmospheric CO in Arctic areas, it should produce seasonal patterns, with higher CO in the summer. Thus, CO levels might have seasonal variations as a function of both photosynthesis activity and contamination by man-made activities. In this regard, CO would be similar to CO<sub>2</sub> which is strongly related to both natural and man-made sources. Figure 2 shows the mean daily concentration of CO and the mean daily CO<sub>2</sub> index without the relatively small manometric correction. The CO<sub>2</sub> concentration data collected during the interval of our research program was obtained from

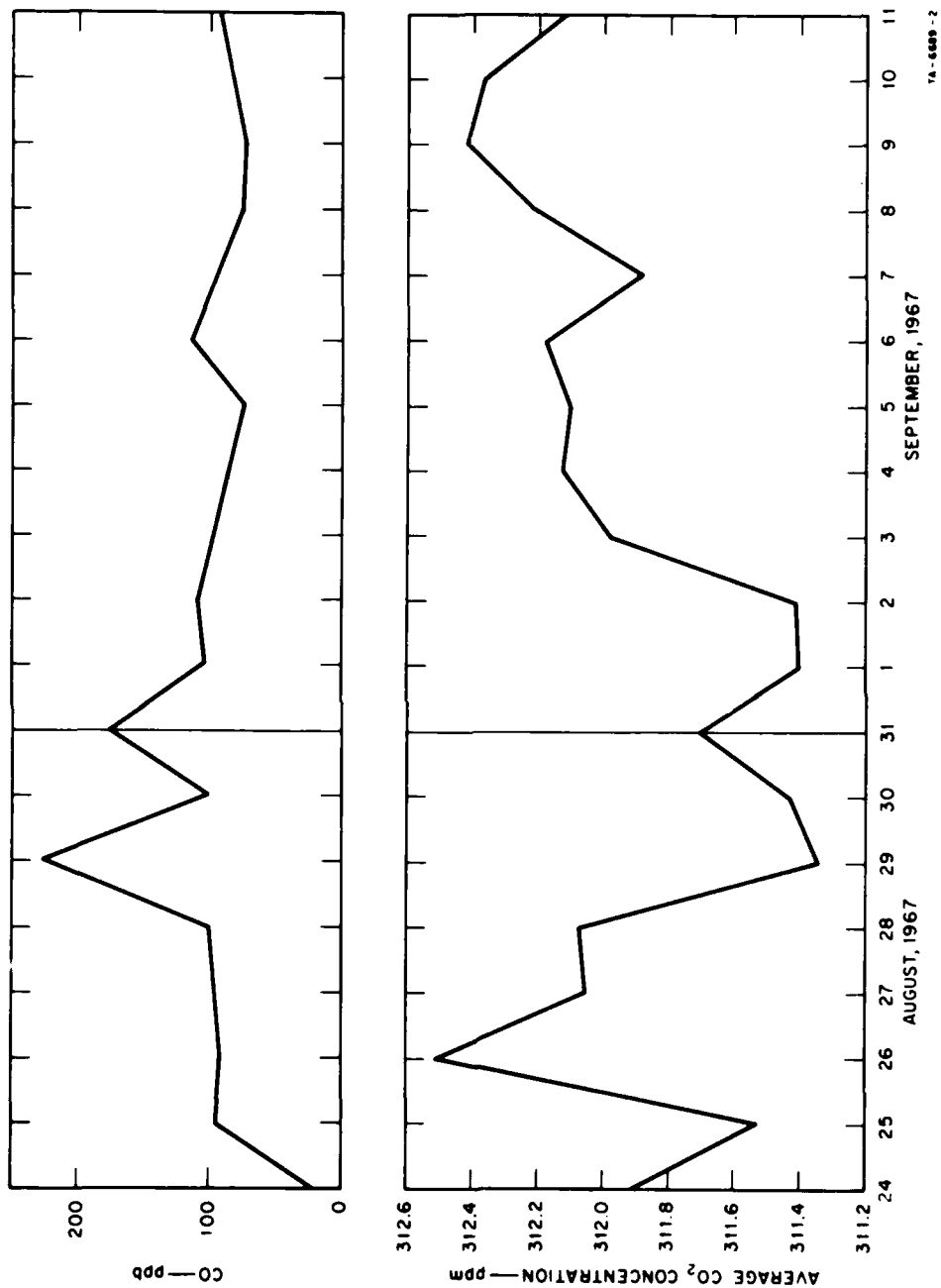


FIG. 2 COMPARISON OF AVERAGE DAILY CARBON MONOXIDE AND CARBON DIOXIDE CONCENTRATIONS, AUGUST 24 — SEPTEMBER 11, 1967

the University of Washington.\* The CO<sub>2</sub> sampling station was located about 100 yards north of the SRI sampling site. Figure 2 does not indicate any obvious correlation between CO<sub>2</sub> and CO concentrations during this period. However, such a short sampling period would indicate only the most obvious of correlations. Figure 3 shows CO concentration variations and CO<sub>2</sub> index values over a 24-hour period on September 2-3, 1967. Again, there is no obvious correlation in diurnal variations with this limited data.

Seasonal variations in CO concentration can only be determined with measurements over longer periods of time and during intervals when variations due to possible natural sources are anticipated.

#### Organic Gas Concentration

Most organic components of the Arctic atmosphere are present at concentrations of 1 ppb or less. The most obvious anomaly in the organic gas measurements is the presence of n-butanol at 100 times the concentration of any other nonmethane organic. This was completely unexpected. Other workers in the field have failed to report the presence of n-butanol in studies of clean atmospheres.<sup>8</sup> Hoff and Kapsalopoulou have reported the presence of lower alcohols and 2-butanol as a component of wood smoke, but n-butanol has not been specifically identified as a component.<sup>9</sup>

Since the presence of n-butanol was considered to be unique, considerable effort, as described previously, was undertaken to establish the validity of our results. The procedures to ensure that n-butanol was neither an artifact nor a result of artificial contamination are summarized as follows:

1. To ensure that n-butanol was not a contaminant of the interior of the wanigan laboratory introduced by error with the air sample,
  - (a) Sample syringes were baked at 125°C for 12 hours--no change noted.

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\* Unpublished data tabulations, University of Washington, Seattle.

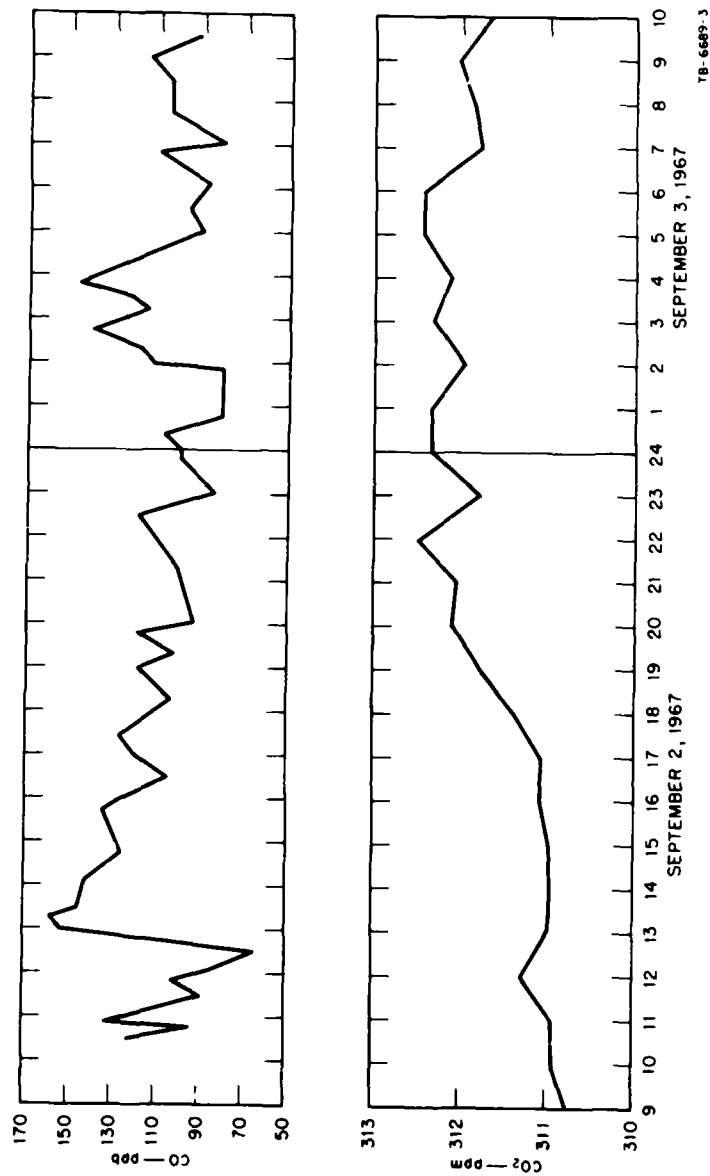


FIG. 3 COMPARISON OF SHORT-TIME VARIATIONS IN CARBON MONOXIDE AND CARBON DIOXIDE CONCENTRATIONS

TB-6689-3

- (b) Carrier gas injected into the gas chromatograph using the same techniques as for sample introduction-- no n-butanol detected.
2. Samples from 50 miles distance contain comparable concentrations of n-butanol; therefore, contamination was not local to area near the wanigan.
  3. Carrier gas + 20% oxygen and nitrogen + 20% oxygen injected into the gas chromatograph did not produce an artifact resembling elution peak of n-butanol.
  4. Sample bottles of Arctic air returned to Menlo Park and chromatographed on the same equipment and under the same conditions contain comparable concentrations of n-butanol. Normal butanol was identified by retention times on three different columns.
  5. Ambient air from Menlo Park does not contain n-butanol at the concentrations found at Point Barrow.
  6. Marine air from Hawaii did not contain n-butanol using the same sample bottles and the same gas chromatographic conditions.

Since the purpose of the research program was to determine the concentration of a broad spectrum of organic contaminants in the Arctic atmosphere, no attempt was made to locate the source of the contaminants. The most probable source of the n-butanol would seem to be a fermentation process of the tundra cover. At least two strains of bacteria, *Clostridium butylicum* and *Clostridium acetobutylicum* are capable of fermenting starch with the production of n-butanol.<sup>10</sup> Other secondary products of fermentation include acetone and ethanol. Optimum fermentation for *Clostridium acetobutylicum* occurs at temperatures of 98 to 107°F. Britton reports that within a few inches of the tundra surface, on sunny summer days, temperatures sometimes reach 100°F or more.<sup>11</sup> This can occur when air temperatures 4 to 5 feet above the ground are only in the high 60's.

Figure 4 illustrates the variation in mean daily concentration of the major organic components of interest tabulated in Table II over the sampling period. With the exception of the unknown, all components were present in minimum concentrations at the beginning and end of the sample period, with maximum concentrations occurring from September 5 to 6. The unknown showed a high concentration peak at the beginning of the sampling period as well. Also included in Fig. 4 are plots of the



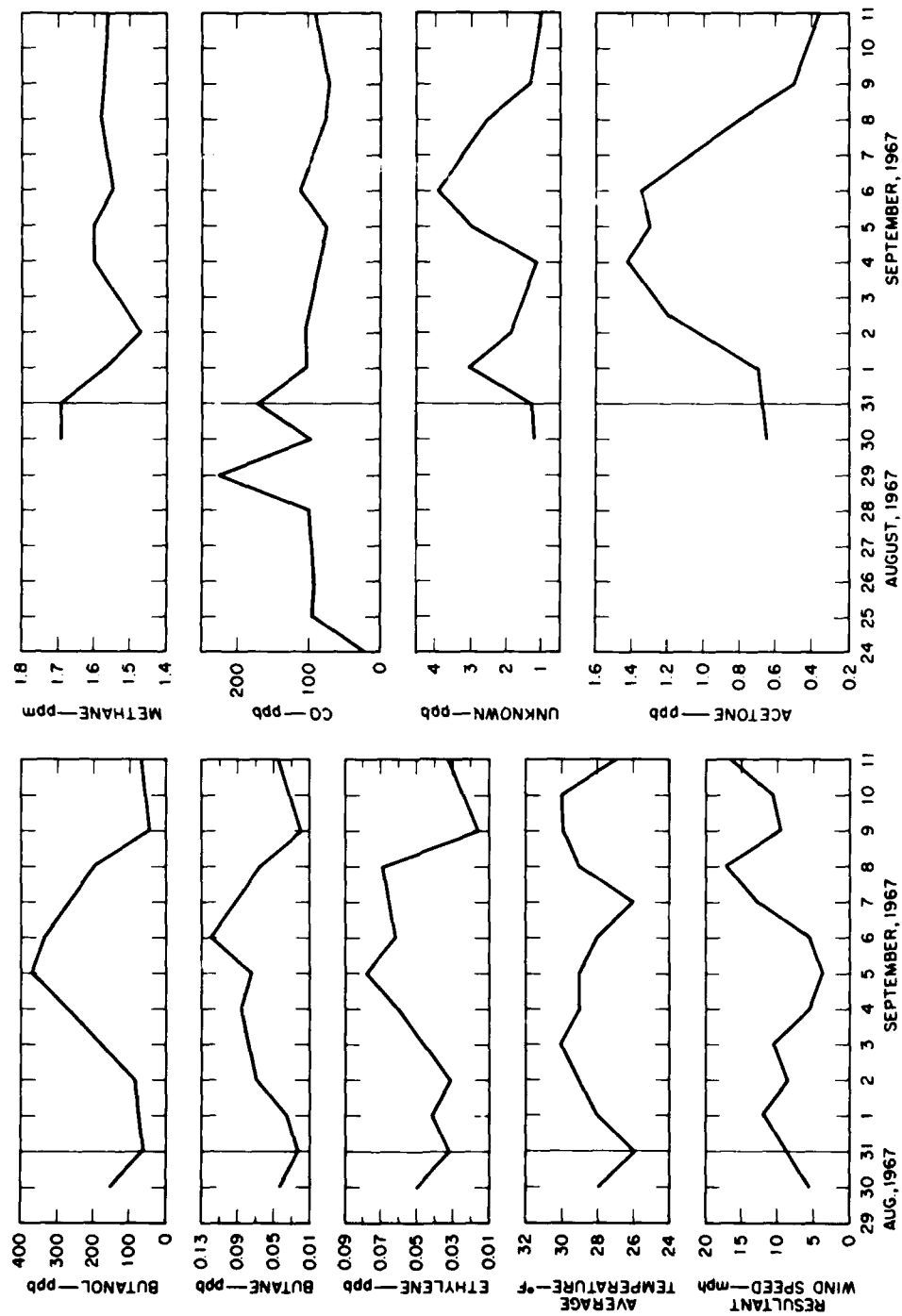


FIG. 4 CONCENTRATION PATTERNS OF ATMOSPHERIC COMPONENTS AND METEOROLOGICAL PARAMETERS

TC-6689-4

resultant wind speed and average daily temperature during the sampling period. The average daily organic concentration patterns all tend to vary in a somewhat similar manner with the maximum similitude occurring with n-butanol and acetone. There are insufficient data to establish any significant correlations of organic concentration variations with seasonal changes.

#### Methane and Condensation Nuclei Concentration

The concentration of methane in the Arctic atmosphere is similar to that measured in other clean atmosphere areas.<sup>1</sup> The mean methane concentration was 1.59 ppm. The estimated world-wide methane concentration is in the range of 1.2 - 1.5 ppm. The presence of natural gas wells and pipelines in the Barrow area could contribute methane through leaks and seepages.

The condensation nuclei concentrations were found to be extremely low and indicative of an atmosphere unpolluted by local combustion sources.

### III. SUGGESTIONS FOR ADDITIONAL FIELD PROGRAM

The initial field program was scheduled to coincide with the period of minimum seasonal levels of carbon dioxide in the atmosphere. Although there is no known cycle that would link  $\text{CO}_2$  to  $\text{CO}$ ,  $\text{CH}_4$ , or the other hydrocarbons, the presence of large concentrations of n-butanol indicates that bacterial processes may contribute significant quantities of organics to the atmosphere concurrent with minimum  $\text{CO}_2$  concentrations.

Since many carbon compounds can be related to various cycles in the biosphere, processes generating n-butanol may also be responsible for many of the organic components present in the Arctic atmosphere. Studies of the chemistry of the Arctic atmosphere should be made over longer durations and at seasons when the photosynthesis activity and the bacterial activity are significantly different from those observed in the present program. In this regard we believe that a complementary field program should be conducted during the month of April (1969), the expected time of maximum  $\text{CO}_2$  concentrations at Point Barrow.

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Investigations have been conducted on the concentrations of carbon monoxide and hydrocarbons of low molecular weight in "clean" Arctic air, and their patterns as functions of meteorological parameters have been interpreted.			

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# STANFORD RESEARCH INSTITUTE



## Main Offices and Laboratories

333 Ravenswood Avenue  
Menlo Park, California 94025  
(415) 326-6200  
Cable: STANRES, Menlo Park  
TWX: 910-373-1246

## Regional Offices and Laboratories

### Southern California Laboratories

820 Mission Street  
South Pasadena, California 91030  
(213) 799-9501 • 682-3901  
TWX: 910-588-3280

### SRI-Washington

1611 North Kent Street, Rosslyn Plaza  
Arlington, Virginia 22209  
(703) 524-2053  
Cable: STANRES, Washington, D.C.  
TWX: 710-955-1137

### SRI-New York

200 E. 42nd Street  
New York, New York 10017  
(212) 661-5313

### SRI-Huntsville

Missile Defense Analysis Office  
4810 Bradford Blvd., N.W.  
Huntsville, Alabama 35805  
(205) 837-3050  
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10 South Riverside Plaza  
Chicago, Illinois 60606  
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### SRI-Europe

Pelikanstrasse 37  
8001, Zurich, Switzerland  
27 73 27 or 27 81 21  
Cable: STANRES, Zurich

### SRI-Scandinavia

Skeppargatan 26  
S-114 52 Stockholm, Sweden  
60 02 26; 60 03 96; 60 04 75

### SRI-Japan

Edobashi Building, 8th Floor  
1-6, Nihonbashi Edobashi  
Chuo-ku, Tokyo  
Tokyo 271-7108  
Cable: STANRESEARCH, Tokyo

### SRI-Southeast Asia

Bangkok Bank Building  
182 Sukhumvit Road  
Bangkok, Thailand  
Bangkok 910-181  
Cable: STANRES, Bangkok

## Representatives

### France

Roger Godino  
94, Boulevard du Montparnasse  
75 Paris 14<sup>e</sup>, France  
633 37 30

### Italy

Lorenzo L. Franceschini  
Via Macedonio Melloni 49  
20129, Milan, Italy  
72 32 46

### Portugal

J. Gasparinho Correia  
Avenida Joao XXI, 22-3 Esq.  
Lisbon, Portugal  
72 64 87